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(54) Title: PROCESS CATALYSED BY BIS-TRIFLIMIDE COMPOUNDS

(57) Abstract: A process for carrying out a chemical reaction which is catalysed by one or more metal or hydrogen fluoroalkyl-sulfonylated compound which process comprises carrying out said reaction in the presence of an ionic liquid or in solvent-free conditions.

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12 **PROCESS CATALYSED BY BIS-TRIFLIMIDE COMPOUNDS**

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14 The present invention relates to a process for

15 carrying out a chemical reaction which is catalysed

16 by bis-triflimide and related bis-trifilimide

17 compounds. More specifically, the present invention

18 relates a process for carrying out such chemical

19 reactions in the presence of an ionic liquid or in

20 solvent-free conditions.

21

22 The catalysis of chemical reactions is of major

23 importance in chemistry. The salts of certain

24 metals are known to act as Lewis acids (electron

25 pair acceptors), which interact with the reactants

26 (and products) of a reaction, producing a reaction

27 rate enhancement and/or selectivity enhancement.

28 Also salts of metals which can exist in variable

29 oxidation states (such as transition metals) are

30 known to catalyse chemical reactions such as

1   Friedel-Crafts, oxidation, reduction, Diels-Alder,
2   isomerisation, coupling, addition and elimination
3   reactions.   The Friedel-Crafts reaction is often
4   used to functionalise aromatic rings. The reaction
5   involves the interaction of an acylating or
6   alkylating agent such as benzoyl chloride or benzyl
7   chloride with an aromatic compound such as benzene
8   to give the products, in this case, benzophenone and
9   diphenylmethane. The reaction requires a Lewis acid
10   catalyst such as aluminium(III) chloride.   The
11   reaction suffers from a major disadvantage in that,
12   particularly with acylation reactions, at least one
13   molar equivalent of Lewis acid catalyst is needed.
14   The work-up of these reactions results in the
15   destruction of the catalyst and can produce
16   considerable amounts of acidic aqueous waste. There
17   is a need for an improved catalyst system which
18   requires less catalyst, produces less waste and
19   allows for the catalyst to be reused and recycled.
20
21   Metal bis-triflimides are known as catalysts for
22   some reactions. Examples include polymerisation of
23   styrene with titanium (or zirconium) bis-triflimides
24   in the solvent toluene.   Magnesium bis-triflimide
25   has been used for the reaction of silyl-enol ethers
26   or silyl-ketene acetals with allylic or benzylic
27   acetates in the solvent dichloromethane.   Scandium
28   bis-triflimide has been used as a catalyst for the
29   formation of acetals and ketals from carbonyl
30   compounds   (or   enol   ethers)   in   the   solvent

1   dichloromethane.   Aluminium, ytterbium and titanium
2   bis-triflimides have been used in the reaction of
3   acetic anhydride with anisole or diphenyl ether to
4   give   acetyl   anisole   or   4-phenoxyacetophenone
5   respectively.   These reactions are carried out in
6   the dangerous and explosive solvent, nitromethane.
7   Such a procedure is of very limited benefit as
8   aromatics less reactive than anisole would require
9   elevated reaction temperatures and can only be
10 carried out on a small scale due to the inherent
11 explosion risk.   There is therefore a need for a
12 reaction system that does not require the use of
13 explosive solvents such as nitromethane or toxic
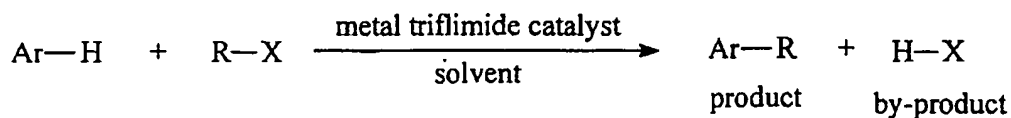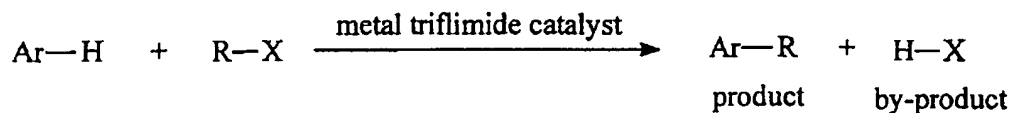14 solvents such as toluene or dichloromethane.
15
16 The present invention solves the problems of the
17 prior art by providing a process for carrying out a
18 chemical reaction which is catalysed by one or more
19 metal   or   hydrogen   fluoralkylsulfonated   compound
20 which process comprises carrying out said reaction
21 in the presence of an ionic liquid or in solvent-
22 free conditions.
23
24 Suitably   the   chemical   reaction   is   an   aromatic
25 electrophillic substitution reaction such as the
26 reaction of an aromatic compound and an alkylating,
27 acylating   or   sulfonating   agent   to   give   an
28 arylalkane, aryl ketone or sulfone.   The reaction
29 may be a Friedel-Crafts acylation, Friedel-Crafts
30 alkylation or a sulfonylation.   The reaction may be

1   the reaction of acid halides, anhydrides or
2   carboxylic acids with aromatic compounds to give an
3   aryl ketone. The reaction can be a reaction of
4   sulfonyl halides, sulfonic anhydrides or sulfonic
5   acids with aromatic compounds to give a sulfone.
6   The reaction may be a reaction of alkenes with
7   aromatic compounds to give aryl alkanes. The
8   reaction may also be a bis-triflimide compound
9   catalysed or promoted isomerisation, polymerisation
10   or rearrangement of chemical compounds or molecules.
11   The reaction may be a rearrangement of esters of
12   phenols to acyl phenols (Fries rearrangement). The
13   reaction may be a dimerisation (or oligiomerisation
14   or polymerisation) of alkenes to give dimerised
15   alkenes (or oligomerised or polymerised alkenes).
16   The reaction can be the migration or isomerisation
17   of carbon-carbon double bonds in unsaturated
18   compounds. The reaction can be an hydration,
19   nitration, carbon-carbon bond forming reaction,
20   halogenation, oxidation or reduction reaction. A
21   general reaction scheme for the reactions catalysed
22   using metal bis-triflimides is shown below:
23

$$\text{Ar}\!-\!\text{H} \;+\; \text{R}\!-\!\text{X} \;\xrightarrow{\text{metal triflimide catalyst}}\; \underset{\text{product}}{\text{Ar}\!-\!\text{R}} \;+\; \underset{\text{by-product}}{\text{H}\!-\!\text{X}}$$

$$\text{Ar}\!-\!\text{H} \;+\; \text{R}\!-\!\text{X} \;\xrightarrow[\text{solvent}]{\text{metal triflimide catalyst}}\; \underset{\text{product}}{\text{Ar}\!-\!\text{R}} \;+\; \underset{\text{by-product}}{\text{H}\!-\!\text{X}}$$

24
25
26

1   where Ar = aromatic group, R = alkyl, acyl,

2   alkylsulfonyl, arylsulfonyl.   X = Cl, OH, Br, I, F,

3   OR, SH, NR$_2$, OSO$_2$R, O$_2$CR   or other leaving group.

4

5   By   metal   or   hydrogen   fluoroalkylsulfonylated

6   compound is mea a compound derived from a metal or

7   hydrogen cation and $[N(SO_2C_xF_{(2x+1)})_2]^-$ anion.   For

8   example, the catalyst can be any compound containing

9   a metal and a fluorinated-alkylsulfonylated anion

10 (preferably a fluorinated-alkylsulfonylamine anion).

11 The   one   or   more   metal   or   hydrogen

12 fluoroalkylsulfonylated   compound   is   preferably   a

13 metal or hydrogen bistriflimide.   By bis-triflimide

14 compound is meant any compound which comprises the

15 ion $[N(SO_2CF_3)_2]^-$. This ion is commonly known by the

16 following   names: triflimide,

17 bis(trifluoromethanesulfonyl)amide,   bis-

18 trifluoromethanesulfonimide,

19 bis(trifluoromethanesulfonyl)imide,

20 trifluoromethanesulfonimide.   In this document, the

21 term bis-triflimide will be used as the name for the

22 $[N(SO_2CF_3)_2]^-$ ion.   Also, the abbreviation [NTf$_2$] is

23 sometimes used to represent the $[N(SO_2CF_3)_2]^-$ ion.

24 Preferably the bis-triflimide compound is a metal

25 bis-triflimide catalyst or hydrogen bis-triflimide

26 HN(SO$_2$CF$_3$)$_2$.   The formula of the hydrogen and metal

27 bistriflimide catalyst is

28

29          $M_x{}^{n+}$ $[\{N(SO_2CF_3)_2\}_{(nx-yz)}]^{(nx-yz)-}$ $L_y{}^{z-}$

30

1   where M is a hydrogen or a metal;

2   L is a negative or neutral ligand;

3   n is 2,3,4,5,6,7 or 8 ;

4   x is greater than or equal to 1

5   y is 0,1,2,3,4,5,6,7or 8; and

6   z is 0, 1,2,3 or 4.

7

8   M may represent more than one type of metal ion. M

9   is preferably a metal selected from the metals in

10 groups 1 to 16 of the periodic table and the

11 lanthanides and the actinides. By group 8 is meant

12 the group containing Fe, Ru, Os, Hs, by group 9 is

13 meant the group containing Co, Rh, Ir, Mt, etc. L

14 may be selected from oxos (such as VO^{2+}), phosphines

15 (such as triphenylphosphine), water, halides or

16 ketones. The ligand may originate from a solvent,

17 reagent or by-product in the reaction mixture for

18 making the catalyst or the reaction mixture in which

19 the catalyst is used.

20

21 The metal or metals may possess one or more neutral

22 or negative ligands (such as triphenylphosphine or

23 oxo (such as in VO_2^+)) or any other ligand such as as

24 oxo, phosphines, water, halide or ketones.

25 Preferably the metal or metals are preferably, but

26 not exclusively, a transition metal, lanthanide or

27 actinide, group 2 (Be, Mg, Ca, Sr, Ba), Group 11

28 (Cu, Ag, Au), Group 12 (Zn, Cd, Hg) Group 13 (B, Al,

29 Ga, In, Tl), Group 14 (Si, Ge, Sn, Pb), Group 15 (P,

30 As, Sb, Bi), Group 16 (S, Se, Te, Po). Preferably

7

1   the metal or metals are preferably, but not
2   exclusively in the +2 oxidation state (eg Co^{2+}), in
3   the +3 oxidation state (eg Al^{3+}) or in the +4
4   oxidation state (eg Ce^{4+}). Cationic species
5   containing charged ligands could also be used (eg
6   UO_2^{2+}, VO^{2+}). Monovalent, pentavalent, heptavalent and
7   hexavalent cationic species may also be used.
8   Particularly preferred metal bis-trflimide compounds
9   which have been prepared and isolated for use in the
10   catalytic reactions of the present invention include
11   magnesium bis-triflimide, calcium bis-triflimide,
12   strontium bis-triflimide, barium bis-triflimide,
13   aluminium bis-triflimide, gallium bis-triflimide,
14   indium bis-triflimide, scandium bis-triflimide,
15   yttrium bis-triflimide, lanthanum bis-triflimide,
16   cerium bis-triflimide, ytterbium bis-triflimide,
17   chromium bis-triflimide, manganese bis-triflimide,
18   iron bis-triflimide, cobalt bis-triflimide, nickel
19   bis-triflimide, copper bis-triflimide, zinc bis-
20   triflimide, silver bis-triflimide, cadmium bis-
21   triflimide, tin bis-triflimide, lead bis-triflimide,
22   and bismuth bis-triflimide.
23
24   Typically, the reactions of the present invention
25   require an amount of bis-triflimide compound is
26   between 0.000001 and 1000 mol %, typically this is
27   between 0.1 and 10 mol %, preferably it is between
28   0.5 and 5 mol % and more preferably this is between
29   between 0.5 and 2 mol %.
30

8

1   The process may involve the addition of the bis-

2   triflimide catalyst to the reactants, e.g. the

3   addition of 1 mol % of $Zn(NTf_2)_2$ to a mixture of an

4   alkylating agent or acylating agent or sulfonylating

5   agent and aromatic compound. This can be carried

6   out either in the presence of an ionic liquid or in

7   solvent-free conditions. When carried out in the

8   presence of an ionic liquid, the catalyst may be

9   dissolved or suspended in an ionic liquid. An ionic

10   liquid is a molten salt that is in a liquid state at

11   the reaction temperature and usually (but not

12   essentially) molten at or near room temperature,

13   i.e, 20 °C. When carried out in solvent-free

14   conditions, the catalyst may be soluble, or

15   partially soluble, in the reactants or products

16   (these can act as both solvent and reagent). The

17   products can be separated from the catalyst at the

18   end of the reaction by distillation or solvent

19   extraction with a solvent that the catalyst is

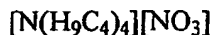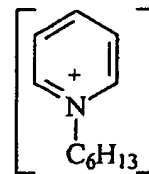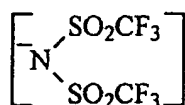20   insoluble in (for example cyclohexane).

21

22   An ionic liquid is a molten salt or mixture of salts

23   that is in the liquid state at the temperature of

24   the reaction. The ionic liquids (if used) are

25   preferably molten salts that are in the liquid state

26   at ambient temperatures, and preferentially dissolve

27   the catalyst when contacted with the reagents.

28   Preferably the catalyst is soluble in the ionic

29   liquid to a much greater extent that the products

30   and/or reactants during the separation of the

9

1   catalyst from the products/reactants. The ionic
2   liquid consists of two components, which are a
3   positively charged cation and a negatively charged
4   anion. Preferably the cation is an organic cation
5   and the anion is an organic or inorganic anion.
6   That cation for the process is preferably a 1-
7   alkylpyridinium (such as 1-hexylpyridinium) or 1,3-
8   dialkylimidazolium cation such as 1-butyl-3-
9   methylimidazolium [bmim] or 1-ethyl-3-
10   methylimidazolium [emim]. Other cations for this
11   process are other alkyl- or poly-alkylpyridinium,
12   alkyl or poly-alkylimidazolium, alkyl or poly-
13   alkylpyrazolium, alkyl or poly-alkyl ammonium, alkyl
14   or poly-alkyl phosphonium, other ammonium,
15   phosphonium cations, alkylated diazabicyclo-[5,4,0]-
16   undec-7-ene and related cations, or any other cation
17   that gives rise to compounds termed ionic liquids.
18   The anion for the process is preferably one that is
19   stable to chemical alteration during the reaction
20   and imparts desirable physical characteristics to
21   the ionic liquid. Some suitable anions for the
22   ionic liquid are bis-trifluoromethanesulfonimide,
23   bis-pentafluoroethanesulfonimide,
24   hexafluorophosphate(V), tetrafluoroborate(III),
25   trifluoromethanesulfonate, cyanamide, fluoro or
26   perfluoroalkylsulfonate, halide, sulfate,
27   hydrogensulfate, alkylsulfate, alkylsulfonate,
28   arylsulfate, arylsulfonate, nitrate, carboxylate,
29   phosphate, hydrogenphosphate, dihydrogenphosphate,
30   alkylphosphate, alkylphosphonate, phosphonate,

1   nitrite,   arsenate,   antimonate,   haloaluminate,

2   aluminate,   borate,   silcate,   haloindate(III),

3   gallate, alkylborate, halogallate or any other anion

4   that gives rise to an ionic liquid.

5   Examples of ionic liquids are given below:

6

$$[H_3C-N\overset{+}{\smile}N-C_2H_5]$$ $$[H_3C-N\overset{+}{\smile}N-C_4H_9]$$ $$\begin{bmatrix} \overset{+}{N} \\ | \\ C_6H_{13} \end{bmatrix}$$

$$\begin{bmatrix} N \overset{SO_2CF_3}{\underset{SO_2CF_3}{\diagup}} \end{bmatrix}$$ $$[PF_6]^-$$ $$[BF_4]^-$$

$$[P(H_9C_4)_4][OSO_2CF_3]$$

7              $$[N(H_9C_4)_4][NO_3]$$

8

9   Preferably the ionic liquid or the catalyst or the

10   ionic liquid and catalyst combination is insoluble

11   in low- or non-polar organic solvents such as

12   diethyl ether or hexane.

13

14   In addition to ionic liquids being excellent media

15   for the execution of the Friedel-Crafts and other

16   reactions, a second major benefit of this invention

17   is that the catalyst and ionic liquid can be

18   recycled and reused in many reactions. This means

19   that catalysts are not lost. This is an improvement

20   over reactions performed in nitromethane, which is

21   an explosive solvent and is hard to recycle.

22

1   The chemical reactions of the present invention may
2   be carried out at temperatures between temperatures
3   of from -100 °C to 450 °C. Preferably the reaction
4   is performed at a temperature between 20 °C and the
5   boiling point of the reactants.
6
7   The present invention further provides a process
8   whereby the bis-triflimide catalyst or related
9   fluoroalkylsulfonylated compound may be generated *in
10 situ* by the addition of a metal or a metal compound
11 (for example, a metal halide) to a bis-triflimide
12 salt (or other bis-triflimide compound) or related
13 fluoroalkylsulfonylated compound. This process can
14 be carried out in the absence of a solvent or in an
15 ionic liquid. An example of this would be the
16 addition of a metal salt to a bis-triflimide ionic
17 liquid (or hydrogen bis-triflimide to an ionic
18 liquid) to generate a catalyst that is capable of
19 catalysing the desired chemical reaction. This can
20 be achieved by taking a metal or metal compound, not
21 necessarily a bis-triflimide salt (for example a
22 metal halide such as, $ZnCl_2$ or $SnCl_4$), and dissolving
23 (reacting) it in a bis-triflimide ionic liquid or
24 other source of bis-triflimide (for example,
25 $HN(SO_2CF_3)_2$). A suitable source of bis-triflimide
26 ions is [emim][NTf_2]. To this combination, the
27 reactants, e.g. alkylating, acylating or sulfonating
28 agent and aromatic compound can be added, with
29 heating if necessary. The products can be separated
30 from the catalyst at the end of the reaction by

1   distillation or solvent extraction with a solvent in

2   which, for example, the catalyst and ionic liquid

3   combination   are   insoluble   (for   example,

4   cyclohexane).

5

6   After the reaction of the present invention, the

7   catalyst   may   be   separated   from   the

8   products/remaining   reactants.   Preferably   the

9   separation process does not destroy the catalyst.

10   When the products of the reactions are aryl ketones,

11   alkyl-aromatic compound, or sulfones, these are

12   usually readily separated from the catalyst or ionic

13   liquid/catalyst mixture by several different means

14   as these are generally neutral covalent molecules.

15   These are usually (but not necessarily) neutral

16   covalent molecules, which are.   The simplest and

17   preferred means is vacuum distillation (typically at

18   1 mm Hg) of the product and by-product directly from

19   the   reaction   vessel   (Kugelrohr   distillation   is

20   preferred but not essential). The catalyst and ionic

21   liquid, having no measurable vapour pressure, remain

22   in the reaction vessel.   The catalyst and/or ionic

23   liquid can be immediately reused upon cooling.   A

24   second valuable method for the separation of the

25   ionic liquid/catalyst from the products is solvent

26   extraction.   The ionic liquid and catalyst are

27   insoluble in low or non-polar organic solvents or

28   supercritical fluids. The reaction vessel can be

29   washed with a solvent or mixture of solvents such

30   that the product and by-product dissolve in the

1 solvent, whereas the ionic liquid and catalyst

2 remain in a separate solution. The separation can

3 be effected by decantation or other means. Suitable

4 solvents for this separation are alkanes

5 (cyclohexane, hexane, petroleum ether or other

6 alkanes or alkane-like compounds), aromatics

7 (toluene, benzene, xylene or other compounds

8 containing an aromatic group), ethers (such as

9 diethyl ether, dibutyl ether) or esters (such as

10 ethyl acetate, amyl acetate), supercritical

11 solvents, or any other material capable of allowing

12 for the separation of the catalyst (and ionic liquid

13 if present) from the products or reagents. Another

14 method involved azeotropic separation with compounds

15 such as steam (for example steam distillation).

16 Some halogenated solvents such as dichloromethane or

17 chloroform partially dissolve the ionic liquid and

18 catalyst and are therefore of lesser use in this

19 process. Thus the present invention provides a

20 process where the product is easily separated from

21 the catalyst or catalyst/ionic liquid combination or

22 solvent containing combination by solvent

23 extraction, distillation, vacuum distillation, steam

24 distillation, pervaporation, azeotropic

25 distillation, precipitation, crystallisation, phase

26 separation, supercritical fluid extraction or any

27 other non-destructive physical process. The present

28 invention further provides a process where the

29 product is easily separated from the catalyst or

30 catalyst / ionic liquid combination or solvent

1   containing combination by solvent extraction using

2   one or more of the following methods: (a) with

3   alkanes or boiling alkanes (eg. cyclohexane at 80

4   °C), (b) vacuum distillation at pressures preferably

5   between 0.01 mmHg and 10 mmHg, (c) steam

6   distillation or with the use of superheated steam at

7   temperatures up to 500 °C, (d) phase separation, (e)

8   supercritical fluid extraction preferably with

9   carbon dioxide.

10

11   The present invention relates to the use of metal

12   bis-triflimides in solvent-free conditions or in

13   ionic liquids. The reactions of aromatics both more

14   and less reactive than anisole can be achieved in

15   this invention, as well as the reaction of anisole

16   itself.   The present invention also provides a

17   method of generating the catalyst in situ thus

18   obviating the need to isolate the metal bis-

19   triflimide catalyst and simplifying the experimental

20   procedure.   One of the principal benefits of this

21   invention is that the product(s) of the reaction can

22   be easily separated from the catalyst and/or ionic

23   liquid - catalyst combination by a physical process

24   such as distillation, steam stripping or by solvent

25   extraction with an inert solvent (including

26   supercritical fluids) or molecular solvents.   The

27   ionic liquid and/or the catalyst (which usually

28   remains in the ionic liquid during the separation

29   process) can be reused for further reactions.

30   Further reactants can simply be added to the ionic

15

1   liquid and/or the catalyst once the previous

2   products/reactants have been removed.

3

4   The present invention is illustrated by the

5   following figures and examples.

6

7   Figure 1 shows the variation of yield with time in

8   the metal bis-triflimide catalysed reaction of

9   benzoyl chloride with toluene.

10

11 Figure 2 shows the variation of yield with time in

12 the 1% $FeCl_3$ and 1% Fe bis-triflimide catalysed

13 reaction of benzoyl chloride with toluene in

14 [bmim][NTf_2].

15

16 Figure 3 shows the variation of yield with time in

17 the synthesis of phenyl-4-chlorophenyl sulfone.

18

19 Figure 4 shows the variation of yield with time for

20 five reaction catalysed by 1 mol% metal chlorides

21 dissolved in [bmim][NTf_2] for the reaction of

22 toluene with benzoyl chloride to give methyl

23 benzophenone at 110°C.

24

25 **Example 1**: The reaction of toluene with benzoyl

26 chloride with cobalt(II) bis-triflimide catalyst.

27

28 Cobalt(II) bis-triflimide (0.13 g, 0.21 mmol) was

29 added to toluene (3.0g, 32.5 mmol) and benzoyl

30 chloride (3.0 g, 21.3 mmol) in a 25 cm^3 round

1   bottomed flask equipped with a magnetic stirrer and

2   reflux condenser.   The mixture was heated under

3   reflux for 3 hours (judged to be at least 99 %

4   complete by gas chromatographic analysis), and

5   cooled to room temperature.   Petroleum ether (15

6   cm^3, bp = 40-60°C) was added and the catalyst

7   precipitated out of solution.   The solution of the

8   product was decanted and the flask washed with a

9   further 15 cm^3 of petroleum ether.   The solvent was

10 evaporated from the combined petroleum ether

11 extracts and the product purified by vacuum

12 distillation (bp = 160-170 °C @ 1 mmHg) in a

13 Kugelrohr apparatus.   This gave methylbenzophenone

14 (4.05 g, 97 % isolated yield).   The catalyst can be

15 reused immediately by adding toluene and benzoyl

16 chloride to the flask (containing the precipitate)

17 and repeating the reaction.

18

19 **Example 2**: The reaction of toluene with benzoyl

20 chloride with cobalt(II) bis-triflimide catalyst in

21 [emim][NTf$_2$].

22

23 Cobalt(II) bis-triflimide (0.13 g, 0.21 mmol) was

24 added   to   1-ethyl-3-methylimidazolium   bis-

25 trifluoromethanesulfonimide ([emim][NTf$_2$]) (2.0 g)

26 in a 25 cm^3 round-bottomed flask equipped with a

27 magnetic stirrer and reflux condenser, and the

28 mixture stirred until the catalyst dissolved.

29 Toluene (3.0g, 32.5 mmol) and benzoyl chloride (3.0

30 g, 21.3 mmol) were added.   The mixture was heated

1 under reflux for 0.5 hours (judged to be at least 99

2 % complete by gas chromatographic analysis), and

3 cooled to room temperature. Petroleum ether (15

4 cm^3, bp = 40-60°C) was added and the catalyst and

5 ionic liquid formed a separate phase. The solution

6 of the product was decanted and the flask

7 (containing the ionic liquid and catalyst) washed

8 three times with 15 cm^3 of petroleum ether. The

9 solvent was evaporated from the combined petroleum

10 ether extracts and the product purified by vacuum

11 distillation (bp = 160-170 °C @ 1 mmHg) in a

12 Kugelrohr apparatus. This gave methylbenzophenone

13 (4.02 g, 96 %). The catalyst and ionic liquid

14 combination can be reused immediately by adding

15 toluene and benzoyl chloride to the flask and

16 repeating the reaction, without loss of activity.

17

18 Examples 1 and 2 show that the acylation of toluene

19 with benzoyl chloride can be carried out with a

20 cobalt(II) bis-triflimide catalyst and that this can

21 be performed with or without an ionic liquid

22 present. However, with the ionic liquid, faster

23 reaction rates are obtained and the catalyst can be

24 recycled more easily. Without the ionic liquid, the

25 products of this reaction are obtained in

26 quantitative yield using 1 mol % catalyst after 3

27 hours heating under reflux (example 1). The

28 reaction time is reduced to 30 minutes when the

29 reaction is carried out in the ionic liquid

18

1   [emim][NTf$_2$] ([emim] = 1-ethyl-3-methylimidazolium)
2   (example 2).
3
4   **Example 3:** The reaction of toluene with benzoyl
5   chloride with nickel(II) bis-triflimide catalyst in
6   [emim][NTf$_2$].
7
8   Nickel(II) bis-triflimide (0.13 g, 0.21 mmol) was
9   added   to   1-ethyl-3-methylimidazolium   bis-
10   trifluoromethanesulfonimide ([emim][NTf$_2$]) (2.0 g)
11   25 cm^3 in a round-bottomed flask equipped with a
12   magnetic stirrer and reflux condenser, and the
13   mixture stirred until the catalyst dissolved.
14   Toluene (3.0g, 32.5 mmol) and benzoyl chloride (3.0
15   g, 21.3 mmol) were added. The mixture was heated
16   under reflux for 1 hour (judged to be at least 99 %
17   complete by gas chromatographic analysis), and
18   cooled to room temperature. Petroleum ether (15
19   cm^3, bp = 40-60°C) was added and the catalyst and
20   ionic liquid formed a separate phase. The solution
21   of the product was decanted and the flask
22   (containing the ionic liquid and catalyst) washed
23   three times with 15 cm^3 of petroleum ether. The
24   solvent was evaporated from the combined petroleum
25   ether extracts and the product purified by vacuum
26   distillation (bp = 160-170 °C @ 1 mmHg) in a
27   Kugelrohr apparatus. This gave methylbenzophenone
28   (4.04 g, 97 % isolated yield). The catalyst and
29   ionic liquid combination can be reused immediately
30   by adding toluene and benzoyl chloride to the flask

1   and   repeating   the   reaction,   without   loss   of

2   activity.

3

4   The   results   from   Examples   2   and   3   are   shown   in

5   Table.

6

7   **Table 1,** The gas chromatographic (GC) yields of

8   benzophenones derived from the reaction of benzoyl

9   chloride with toluene with 1% metal bis-triflimide

10 catalyst in [emim] [NTf$_2$].

Compound	Yield	Time / h
Co(NTf$_2$)$_2$	99	0.5
Ni(NTf$_2$)$_2$	99	1

11

12 **Example 4**

13 Anisole (0.30 cm^3, 2.8 mmol), acetic anhydride (0.50

14 cm^3, 5.0 mmol), M(NTf$_2$)$_n$ catalyst (0.1375 mmol (M =

15 Al, n=3; M = Zn, n = 2; M = Yb, n = 3; M = Y, n =

16 3)) were dissolved in the ionic liquid [bmim] [PF$_6$].

17 These four reactions were heated at 30 °C for 24

18 hours. The course of the reaction was determined by

19 HPLC analysis of the reaction mixture and the yields

20 are shown in Table 2.

21

22 **Table 2,** The variation of GC yield with time for

23 the acetylation of anisole with acetic anhydride

24 with metal bis-triflimide catalysts in [bmim] [PF$_6$].

25

26

27

Catalyst	% Yield (35 min)	% Yield (115 min)	% Yield (245 min)	% Yield (1375 min)
Al(NTf$_2$)$_3$	45	55	61	63
Zn(NTf$_2$)$_3$	23	36	44	61
Yb(NTf$_2$)$_3$	49	61	64	69
Y(NTf$_2$)$_3$	55	62		71

1

2 **Example 5**

3 Anisole (0.50 cm^3, 4.6 mmol), benzoic anhydride

4 (1.15 g, 5.06 mmol), M(NTf$_2$)$_n$ catalyst (0. 23 mmol (M

5 = Al, n=3, 0.20 g; M = Ce, n = 4, 0.29 g)) were

6 dissolved in the ionic liquid [bmim][NTf$_2$] (2.0 g).

7 These two reactions were heated at 60 °C for 24

8 hours. The course of the reaction was determined by

9 gas chromatographic analysis of the reaction mixture

10 and the yields are shown in Table 3.

11

12 **Table 3,** The variation of GC yield with time for

13 the benzoylation of anisole with benzoic anhydride

14 with metal bis-triflimide catalysts in [bmim][PF$_6$].

15

Catalyst	% Yield (60 min)	% Yield (120 min)	% Yield (180 min)	% Yield (1350 min)
Al(NTf$_2$)$_3$	44	62	67	68
Ce(NTf$_2$)$_4$	32	49	56	84

16

17 **Example 6**

18 Fluorobenzene (5.77 g, 60 mmol), 4-fluorobenzoyl

19 chloride (4.75 g, 30 mmol), ZnCl$_2$ (1.36 g, 10 mmol)

20 and [emim][NTf$_2$] were placed in an autoclave and

21 heated with stirring for 48 hours at 160 °C. The

1   reactor was cooled and the pressure (HCl gas)

2   released. Gas chromatographic analysis showed that

3   a 99 % conversion to a mixture of 2,4'-

4   difluorobenzophenone,   3,4'-difluorobenzophenone,

5   4,4'-difluorobenzophenone in 17 : 8 : 75 ratio

6   respectively.   The difluorobenzophenones were

7   isolated by solvent extraction with petroleum ether

8   (bp = 40 - 60 °C), followed by evaporation of the

9   solvent. The ionic liquid / zinc chloride catalyst

10 system could be used in further reactions, with

11 similar activity.   This result shows that the

12 classically   unreactive   aromatic   compound

13 fluorobenzene can be acylated with 4-fluorobenzoyl

14 chloride to give isomers of 2-, 3-, or 4-4'-

15 difluorobenzophenone in [emim][NTf₂] using an *in*

16 *situ* zinc catalyst. This catalyst was generated by

17 dissolving zinc(II) chloride in the [emim][NTf₂]

18 ionic liquid. The reaction gave a 95 % yield (17 :

19 8 : 75 *o*-, *m*-, *p*- isomer ratio).

20

21 **Example 7**

22 Benzoic acid (0.31 g, 2.5 mmol), *m*-xylene (0.53 g,

23 5.0 mmol), [bmim][NTf₂] (0.50 g) and M(NTf₂)₂ (M = Co

24 (0.14 g, 0.25 mmol), or Zn (0.15 g, 0.25 mmol) were

25 placed in flasks equipped with stirrers and

26 condensers. The contents of the flask were heated

27 under reflux (*ca* 140 - 150 °C) for 2 days, then

28 cooled to room temperature. The products were

29 analysed by gas chromatographic analysis and found

30 to give 93 and 87 % conversions (for Co and Zn bis-

1   triflimide   reactions   respectively)   to   2,4-

2   dimethylbenzophenone and, it is believed to be, 2,6-

3   dimethylbenzophenone (11 : 1 isomer ratio in both

4   cases). The results show that Zinc and cobalt bis-

5   triflimide   have   been   found   to   catalyse   the

6   benzoylation of m-xylene with benzoic acid.   The

7   reaction is slower that the corresponding reaction

8   with benzoyl chloride. The catalyst was recycled and

9   the   reaction   was   repeated.   The   results   of   the

10   repeat experiment are shown in Table 4.

11

12   **Table 4,** The yields of benzophenones derived from the

13   reaction of benzoic acid with m-xylene with 10%

14   recycled   metal   bis-triflimide   catalyst   in

15   [bmim][NTf$_2$] at 140 °C for 48 hours.

Compound	% Yield	2,4- to 2,6- ratio
Zn(NTf$_2$)$_2$	40	11 : 1
Co(NTf$_2$)$_2$	82	11 : 1

16

17   These are remarkable results given the low

18   reactivity of benzoic acid.   It is to be noted that

19   this reaction produces water as a byproduct and as

20   such it is a very environmentally friendly reaction.

21   Furthermore, it utilises a non corrosive starting

22   material (benzoic acid) and therefore is an safer

23   reaction to perform than the corresponding reaction

24   with benzoyl chloride.   It can be concluded that

25   this is a superior way to produce

26   dimethylbenzophenone.

27

1 **Example 8**: The reaction of toluene with benzoyl

2 chloride with zinc(II) or copper(II) bis-triflimide

3 catalyst in [emim][NTf$_2$].

4

5 Copper or zinc (II) bis-triflimide (0.13 g, 0.21

6 mmol) was added to a mixture of toluene (3.0g, 32.5

7 mmol) and benzoyl chloride (3.0 g, 21.3 mmol). The

8 mixture was heated under reflux for 72 hours (the

9 reaction was monitored by gas chromatographic

10 analysis, by taking a drop of the reaction mixture

11 and suspending it in petroleum ether (b.p. = 40-

12 60°C) and filtering off the catalyst. The starting

13 materials and products, which are soluble in the

14 petroleum ether extract, were cooled to room

15 temperature. Petroleum ether (15 cm^3, bp = 40-60°C)

16 was added and the catalyst and formed a separate

17 phase. The solution of the product was decanted and

18 the flask (containing the catalyst) washed three

19 times with 15 cm^3 of petroleum ether. The solvent

20 was evaporated from the combined petroleum ether

21 extracts and the product purified by vacuum

22 distillation (bp = 160-170 °C @ 1 mmHg) in a

23 Kugelrohr apparatus. This gave methylbenzophenone

24 (4.0 g, 95 %). The catalyst can be reused

25 immediately by adding toluene and benzoyl chloride

26 to the flask and repeating the reaction, without

27 loss of activity. The yields as determined by gas

28 chromatographic analysis are shown in Table 5.

29

1   **Table 5,** the yields of benzophenones derived from the

2   reaction of benzoyl chloride with toluene with 1 %

3   copper(II) or 1 % zinc(II) bis-triflimide catalysts.

4   The figure in brackets refers to the *o-*, *m-* and *p-*

5   isomer ratios.

Time / h	Yield with $Zn(NTf_2)_2$	Yield with $Cu(NTf_2)_2$
24	83	52
48	99 (22 : 1 : 77)	
72		99 (20 : 2 : 78)

6.

7   Zinc(II) and copper(II) bis-triflimide compounds were

8   found to be effective acylation catalysts for the

9   benzoylation of toluene.

10

11 **Example 9:** The reaction of *o-*xylene with benzoyl

12 chloride with an aluminium(III) bis-triflimide

13 catalyst.

14

15 Aluminium (III) bis-triflimide (0.10 g) was added to

16 a mixture of *o-*xylene (3.0g, 28.2 mmol) and benzoyl

17 chloride (3.0 g, 21.3 mmol). The mixture was heated

18 at 120 °C for 18 hours (the reaction was monitored

19 by gas chromatographic analysis, by taking a drop of

20 the reaction mixture and suspending it in petroleum

21 ether (b.p. = 40-60°C) and filtering off the

22 catalyst. The starting materials and product are

23 soluble in the petroleum ether extract), and cooled

24 to room temperature. Petroleum ether (15 cm^3) was

25 added and the catalyst and formed a separate phase.

1 The yields as determined by gas chromatographic
2 analysis was 99% with a 6.0 : 1   3,4- to 2,3-
3 dimethylbenzophenone isomer ratio.   Aluminium(III)
4 bis-triflimide was found to be an effective catalyst
5 for the benzoylation of o-xylene.   The reaction gave
6 a   quantitative   yield   of   two   isomers   of   the
7 corresponding benzophenone (6 : 1   3,4- to 2,3-
8 isomer ratio) after 18 h at 120 °C, using 1 mol % of
9 catalyst.
10
11 **Example 10**: The reaction of toluene with benzoyl
12 chloride with metal bis-triflimide catalyst.
13
14 Various metal (1-ethyl-3-methylimidazolium, Li, Mg,
15 Ca, Mn, Co, Ni, Cu, Zn, Sn, Pb, Al) bis-triflimide
16 salts (1 mol %) was added to a mixture of toluene
17 (3.0g, 32.6 mmol) and benzoyl chloride (3.0 g, 21.3
18 mmol).   The mixture was heated at 110 °C for up to
19 120 hours. The reaction was monitored at regular
20 intervals by gas chromatographic analysis and the
21 reaction stopped when the reaction was judged to be
22 99 % complete by cooling to room temperature.
23 Petroleum ether (15 cm^3) was added and the catalyst
24 and formed a separate phase.   The product was
25 isolated be decanting the petroleum ether extract,
26 followed by Kugenrohr distillation at 1 mm Hg.   The
27 yields after various time intervals are given in
28 Table 6.   The product formed is methylbenzophenone.
29 In all these reactions, the isomer ratio was found to
30 be approximately 76 % *para* and 24 % *ortho*.   This

1 results are shown in Table 6.   Table 1 lists the

2 times required for Co and Ni bis-triflimide in

3 [emim][NTf$_2$].

4

5 **Table 6,** The yields of benzophenones derived from the

6 reaction of benzoyl chloride with toluene with 1%

7 metal bis-triflimide catalyst.

Compound	Yield / %	Time / h
[emim][NTf$_2$]	< 1	48
Li NTf$_2$	< 5	120
Mg(NTf$_2$)$_2$	99	48
Ca(NTf$_2$)$_2$	< 5	120
Mn(NTf$_2$)$_2$	99	5
Co(NTf$_2$)$_2$	99	3
Ni(NTf$_2$)$_2$	99	4
Cu(NTf$_2$)$_2$	99	72
Zn(NTf$_2$)$_2$	99	48
Sn(NTf$_2$)$_2$	55	48
Pb(NTf$_2$)$_2$	95	6
Al(NTf$_2$)$_3$	99	24

8

9 From Table 6, a remarkable difference in reactivity

10 between the compounds chosen is observed. Of these,

11 four compounds appear to have unexpectedly high

12 reactivity, namely those of manganese, cobalt,

13 nickel and lead, whereas compounds such as zinc bis-

14 triflimide and aluminium bis-triflimide have

15 relatively modest activity.   This is completely

16 different to "conventional Friedel-Crafts chemistry"

17 which would suggest that the Al bistriflimide should

1   be the best catalyst. Of particular remark is the

2   catalytic reactivity of Co and Pb. Lithium and

3   calcium bis-triflimide in contrast show very poor

4   activity and with [emim] [bis-triflimide], little or

5   no reaction was observed.

6

7   **Example 11:** The reaction of chlorobenzene with

8   benzoyl chloride with nickel(II) bis-triflimide

9   catalyst in [bmim] [NTf$_2$].

10

11   Nickel(II) bis-triflimide (0.062 g, 0.1 mmol) was

12   added to 1-butyl-3-methylimidazolium bis-

13   trifluoromethanesulfonimide ([bmim] [NTf$_2$]) (1.0 g)

14   in a 25 cm^3 round-bottomed flask equipped with a

15   magnetic stirrer and reflux condenser, and the

16   mixture stirred until the catalyst dissolved.

17   Chlorobenzene (1.68 g, 15 mmol) and benzoyl chloride

·18   (1.41 g, 10 mmol) were added. The mixture was

19   heated under reflux for 72 hours and was analysed by

20   gas chromatographic analysis as in previous

21   examples. The reaction was cooled to room

22   temperature. Petroleum ether (15 cm^3, bp = 40-60°C)

23   was added and the catalyst and ionic liquid formed a

24   separate phase from the petroleum ether layer. The

25   solution of the product (in petroleum ether) was

26   decanted and the flask (containing the ionic liquid

27   and catalyst) washed three times with 15 cm^3 of

28   petroleum ether. Concentration of the organic

29   extract, followed by Kugenrohr distillation at 1 mm

30   Hg (bp = 170-190 °C), gave chlorobenzophenone (1.65

28

1   g, 74 %). GC analysis showed 78 % yield after 72

2   hours, with a 70 : 8 4- to 2- isomer ratio. This is

3   a remarkable result, as chlorobenzene is known to be

4   classically unreactive in acylation reactions. It

5   has not previously been possible to isolate

6   significant quantities of the products of the

7   acylation of chlorobenzene.

8

9   **Example 12:** The reaction of chlorobenzene with

10   benzoyl chloride with cobalt(II) bis-triflimide or

11   zinc(II) bis-triflimide catalyst in [bmim][NTf$_2$].

12

13   In two separate reactions, either zinc(II) bis-

14   triflimide (0.16 g, 5 mol %) or cobalt(II) bis-

15   triflimide (0.15 g, 5 mol %) was added to 1-butyl-3-

16   methylimidazolium   bis-trifluoromethanesulfonimide

17   ([bmim][NTf$_2$]) (1.0 g) 25 cm^3 in a round-bottomed

18   flask equipped with a magnetic stirrer and reflux

19   condenser, and the mixture was heated gently and

20   stirred   until   the   catalyst   dissolved.

21   Chlorobenzene (0.68 g, 6 mmol) and benzoyl chloride

22   (0.72 g, 5 mmol) were added. The mixture was heated

23   under reflux for 18 hours and was analysed by gas

24   chromatographic analysis as in previous examples.

25   The reaction was cooled to room temperature.

26   Cyclohexane (15 cm^3) was added and the catalyst and

27   ionic liquid formed a separate phase. The solution

28   of the product was decanted and the flask

29   (containing the ionic liquid and catalyst) washed

30   three times with 15 cm^3 cyclohexane followed by

1 Kugelrohr distillation at 1 mm Hg (bp = 180-200 °C).

2 This gave a mixture of 2- and 4-chlorobenzophenone.

3 GC yield = 97 % (6.8 : 1 *p-* to *o-* isomer ratio) for

4 cobalt catalyst and 55 % GC yield (6.5 : 1 *p-* to *o-*

5 isomer ratio) for the zinc catalyst.

6

7 The reaction of chlorobenzene with benzoyl chloride

8 was investigated, as chlorobenzene is much more

9 difficult to acylate. Although reasonable yields

10 could be obtained with 1 mol % catalyst, it was

11 found that 5-mol % catalyst gave more acceptable

12 reaction rates. The reaction was found to be 95 %

13 complete with cobalt bis-triflimide after 18 hours

14 and 55 % complete with zinc bis-triflimide (Table

15 7). The catalyst was found to be less active after

16 extracting the product with boiling cyclohexane and

17 recycling the ionic liquid / catalyst. The activity

18 of the catalyst was restored by adding a trace of

19 hydrogen bis-triflimide (0.1 mol %).

20

21 **Table 7,** The yields of benzophenones derived from the

22 reaction of benzoyl chloride with chlorobenzene with

23 5% metal bis-triflimide catalyst in [bmim][NTf$_2$].

Compound	Yield	Time / h
Co(NTf$_2$)$_2$	95	18
Zn(NTf$_2$)$_2$	55	18

24

25 **Example 13:** The reaction of toluene with benzoyl

26 chloride with hydrogen and metal bis-triflimide

27 catalyst.

1

2   Various   metal   bis-triflimide   compounds: Sr(II),

3   Ba(II),   In(III),   In(III)   in   [bmim][NTf$_2$],   Cr(III),

4   Ce(IV),   Yb(III),   and   hydrogen   bis-triflimide

5   {HN(SO$_2$CF$_3$)$_2$}   (1 mol %)   were   added   to   a   mixture   of

6   toluene   (1.38 g,   15.0 mmol)   and   benzoyl   chloride

7   (1.41 g,   10.0 mmol).   The   mixture   was   heated   at   110

8   °C   for   up   to   120   hours.   The   reaction   was   monitored

9   at   various   intervals   by   gas   chromatographic   analysis

10   and   the   reaction   stopped   after   5   days.   The   yields

11   of   methylbenzophenone   with   respect   to   time   are   shown

12   in   Figure   1.   The   reaction   of   benzoyl   chloride   and

13   toluene   gave   2-   and   4-methylbenzophenone.   All   these

14   compounds   were   found   to   be   active   Friedel-Crafts

15   catalysts,   but   with   considerably   different

16   activities.   Of   these,   the   activities   of   indium(III)

17   and   iron(III)   (Example   14)   are   the   most   notable,   as

18   they   are   exceptionally   good   catalysts.   The p-   to o-

19   selectivities   were   in   the   range   3.9   to   4.4   to   1,

20   with   the   indium   and   iron   catalysts   giving   4.4   :   1

21   selectivity.

22

23   **Example 14**: The   reaction   of   toluene   with   benzoyl

24   chloride   with   iron(III)   bis-triflimide   or   iron(III)

25   chloride   dissolved   in   [bmim][NTf$_2$].

26

27   In   two   separate   reactions,   either   iron(III)   bis-

28   triflimide   (1 mol %)   or   iron(III)   chloride   (1 mol %)

29   was   added   to   1-butyl-3-methylimidazolium   bis-

30   trifluoromethanesulfonimide   ([bmim][NTf$_2$])   (1.0   g)

1   25 cm^3 in a round-bottomed flask equipped with a

2   magnetic stirrer and reflux condenser, and the

3   mixture was heated gently and stirred until the

4   catalyst dissolved.   Toluene (1.38 g, 15 mmol) and

5   benzoyl chloride (1.41 g, 10 mmol) were added.   The

6   mixture was heated under reflux for 48 hours and was

7   analysed by gas chromatographic analysis as in

8   previous examples. The yield of methylbenzophenone

9   with respect to time is shown in Figure 2.   Here,

10   the activity of the iron catalyst was tested in two

11   separate ways: (a) with 1% FeO(NTf$_2$) in [bmim][NTf$_2$]

12   and (b) 1% FeCl$_3$ in [bmim][NTf$_2$].   In both cases, the

13   activity and selectivity were similar, indicating

14   that FeCl$_3$ and FeO(NTf$_2$) are possibly precursors to

15   catalyst, when dissolved in excess [bmim][NTf$_2$].

16

17   **Example 15**: The reaction of toluene with methane

18   sulfonyl chloride with zinc(II) bis-triflimide.

19

20   Zinc(II) bis-triflimide (0.13 g, 2.5 mol %) was

21   added to a round-bottomed flask equipped with a

22   magnetic stirrer and reflux condenser.   Toluene

23   (1.38 g, 15 mmol) and methane sulfonyl chloride

24   (1.14 g, 10 mmol) were added.   The mixture was

25   heated under reflux for 24 hours and was analysed by

26   gas chromatographic analysis as in previous

27   examples.   All the methane sulfonyl chloride had

28   reacted and three isomers of (2-, 3- and 4-

29   methylphenyl)methylsulfone had formed (yield = 99

30   %), isomer ratio = 35 : 18 : 47 for the *o-*, *m-* and

1   p- isomers.   The product was extracted from the

2   catalyst by dissolving it in cyclohexane (20 cm^3)

3   followed by decantation of the cyclohexane extract.

4   The catalyst was washed with cyclohexane (2 x 20

5   cm^3) and the combined cyclohexane extracts were

6   concentrated on a rotary evaporator.   The product

7   was Kugelrohr distilled at 100-110°C to give 1.62 g

8   of a colourless oil (96 % isolated yield).

9

10   **Example 16:** The reaction of benzene with benzene

11   sulfonyl chloride with zinc(II) bis-triflimide.

12

13   Zinc(II) bis-triflimide (0.062 g, 1 mol %) was

14   dissolved in [bmim][NTf$_2$] (1.0 g) in a round-

15   bottomed flask equipped with a magnetic stirrer and

16   reflux condenser.   Benzene (1.56 g, 20 mmol) and

17   benzene sulfonyl chloride (1.76 g, 10 mmol) were

18   added.   The mixture was heated under reflux for 18

19   hours and was analysed by gas chromatographic

20   analysis as in previous examples.   All the benzene

21   sulfonyl chloride had reacted diphenyl sulfone had

22   formed (yield = 99 %).   The product was extracted

23   from the catalyst and ionic liquid by dissolving it

24   in boiling cyclohexane (5 x 30 cm^3) followed by

25   decantation of the cyclohexane extract.   The

26   diphenylsulfone crystalised on cooling and was

27   collected by filtration (2.03 g, 93 % isolated

28   yield).   The reaction of benzene with benzene

29   sulfonyl chloride gave the expected diphenyl sulfone

30   in 99% yield with a Zn(NTf$_2$)$_2$ catalyst (18 h at

33

1 reflux).   The diphenyl sulfone was extracted with

2 boiling cyclohexane and the ionic liquid and

3 catalyst could be reused.

4

5 **Example 17**: The reaction of *m*-xylene with benzene

6 sulfonyl chloride with zinc(II) bis-triflimide.

7

8 Zinc(II) bis-triflimide (0.062 g, 1 mol %) was

9 dissolved in [bmim][NTf$_2$] (1.0 g) in a round-

10 bottomed flask equipped with a magnetic stirrer and

11 reflux condenser and *m*-xylene (2.12 g, 20 mmol) and

12 benzene sulfonyl chloride (1.76 g, 10 mmol) were

13 added.   The mixture was heated under reflux for 18

14 hours and was analysed by gas chromatographic

15 analysis as in previous examples. All the benzene

16 sulfonyl chloride had reacted and mostly 2,4-

17 dimethyldiphenylsulfone had formed (yield = 99 %, 20

18 : 1 isomer ratio (by NMR)). The major product is

19 shown below, the structure of the minor isomer is

20 not known but is believed to be the 2,6-dimethyl

21 isomer.

22

23
24
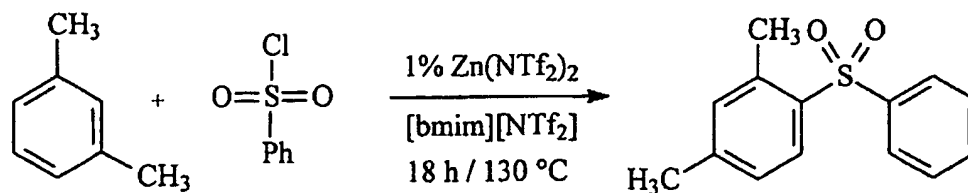
25 The product was extracted from the catalyst and

26 ionic liquid by dissolving it in boiling cyclohexane

27 (5 x 30 cm^3) followed by decantation of the

1   cyclohexane   extract.   The   2,4-

2   dimethyldiphenylsulfone crystalised on cooling and

3   was collected by filtration.

4

5   **Example 18**: The reaction of chlorobenzene with

6   benzene sulfonyl chloride with metal bis-triflimide

7   catalysts.

8

9   In three separate reactions, either magnesium(II)

10 bis-triflimide (0.058 g, 0.1 mol), aluminium(III)

11 bis-triflimide (0.87 g, 0.1 mmol) or cobalt(II) bis-

12 triflimide (0.062 g, 0.1 mmol) was dissolved in

13 [bmim][NTf$_2$] (0.5 g) in a round-bottomed flask

14 equipped with a magnetic stirrer and reflux

15 condenser. Chlorobenzene (1.68 g, 15 mmol) and

16 benzene sulfonyl chloride (1.76 g, 10 mmol) were

17 added. The mixture was heated under reflux for 144

18 hours and monitored by gas chromatographic analysis

19 as in previous examples. The yields with respect to

20 time are given in Figure 3. The product was

21 extracted from the catalyst and ionic liquid by

22 dissolving it in boiling cyclohexane (4 x 10 cm^3)

23 followed by decantation of the cyclohexane extract.

24 The 2- and 4-chlorodiphenylsulfone (9:1 *p-* to *o-*

25 isomer ratio) crystalised on cooling and was

26 collected by filtration. The selectivity was 9:1 for

27 the *p-* isomer and the *o-* isomer was the minor isomer

28 in all cases. Coincidently, the reaction of benzoyl

29 chloride with chlorobenzene also gave the same

30 selectivity and similar reaction rates. Phenyl-4-

1 chlorophenylsulfone is an insecticide. The reaction
2 was found to be slow using 1 mol % catalyst, but 5
3 mol % catalyst gave acceptable reaction rates. The
4 metal salts chosen were aluminium(III), cobalt(II)
5 and magnesium(II) bis-triflimide, in the ionic
6 liquid [bmim][NTf$_2$]. All three catalysts were found
7 to be effective for this reaction. The reaction is
8 shown below.
9
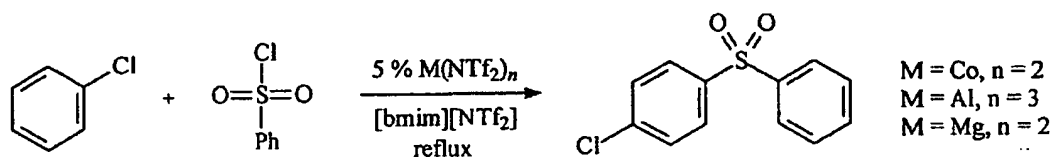
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12

13 **Example 19**: The reaction of benzene with oct-1-ene
14 with nickel(II) bis-triflimide.
15

16 Nickel(II) bis-triflimide (0.06 g, 0.1 mmol) was
17 dissolved in [bmim][NTf$_2$] (1.0 g) in a round-
18 bottomed flask equipped with a magnetic stirrer and
19 reflux condenser. Benzene (3.90 g, 50 mmol) and
20 oct-1-ene (1.12 g, 10 mmol) were added. The mixture
21 was heated under reflux for 18 hours and was
22 analysed by gas chromatographic analysis as in
23 previous examples. The oct-1-ene peak disappeared
24 and three isomers of octylbenzene were formed (70 %,
25 20:26:54 2- to 3- to 4- isomer ratio) as well as
26 octene dimer (30 %). The less dense product phase
27 was decanted from the ionic / catalyst phase and
28 purified by Kugelrohr distillation. The ionic

36

1 liquid and catalyst were prepared for reuse by
2 heating at 60 °C under vacuum for 1 hour. The ionic
3 liquid and catalyst were used for further reactions
4 of benzene with oct-1-ene without loss of activity.
5 This is an alkylation of benzene with an alkene
6 using a metal bis-triflimide catalyst. Benzene and
7 oct-1-ene react in the presence of 1% nickel(II)
8 bis-triflimide in [bmim][NTf$_2$] to form three isomers
9 of octyl benzene and a small amount of hexadecene
10 (unknown isomeric distribution). This reaction
11 shown below:
12
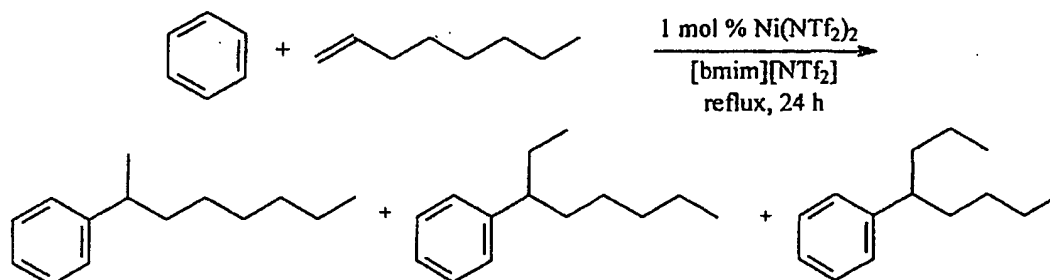
13
14 The alkylation of benzene with oct-1-ene.
15 The reaction gave a 70 % yield (by GC) of three
16 isomers of octylbenzene. The isomer ratio was
17 determined to be 0.75 : 1.00 : 2.03, with the 4-
18 phenyloctene as the major product and 2-phenyloctene
19 as the minor product. During the course of the
20 reaction, isomeration of oct-1-ene to a number of
21 isomers of octene was observed, and the rate of this
22 isomerisation process was considerably faster that
23 the alkylation reaction. It was found that the ionic
24 liquid / catalyst combination remained active on a

1   second run.   To confirm that the minor product of

2   the reaction was an octene dimer, the same reaction

3   was performed, but without any benzene present

4   (shown below).

5

The dimerisation of oct-1-ene.
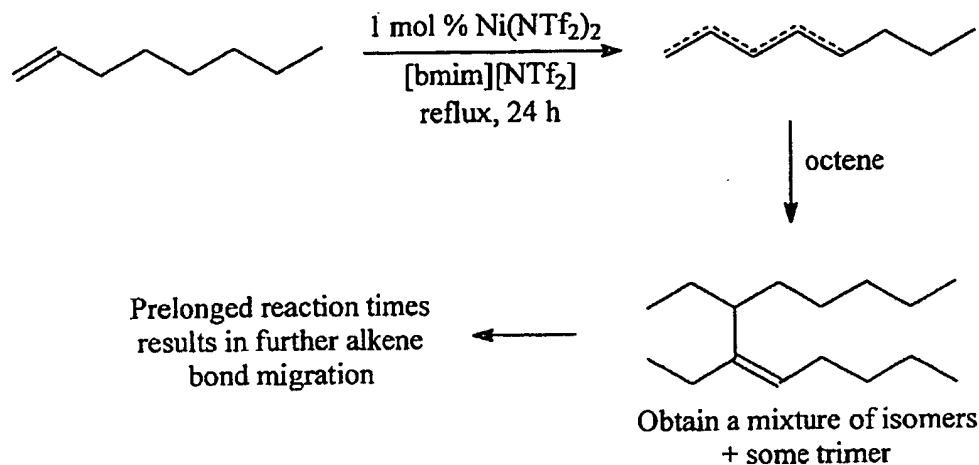
6

7   The dimerisation of oct-1-ene.

8

9   The reaction proceeded initially with isomerisation

10 of octene to a mixture of 4 isomers of octene.

11 After 18 hours, the reaction was almost complete (>

12 95 % conversion). The products were a large number

13 of isomers of dimerised and trimerised octene.   As

14 the reaction was left to run for 6 days, a

15 broadening of the cluster of GC peaked for the dimer

16 and trimer was observed, indicating that further

17 isomerisation was occurring.

18

19 **Example 20**: The dimerisation of oct-1-ene with

20 nickel(II) bis-triflimide.

1

2   Nickel(II) bis-triflimide (0.062 g, 0.1 mmol) was

3   dissolved in [bmim][NTf₂] (0.5 g) in a round-

4   bottomed flask equipped with a magnetic stirrer and

5   reflux condenser.   Oct-1-ene (1.12 g, 10 mmol) was

6   added.   The mixture was heated under reflux for 18

7   hours and was analysed by gas chromatographic

8   analysis as in previous examples. The oct-1-ene peak

9   disappeared and three isomers of octene (oct-2-ene,

10   oct-3-ene and oct-4-ene) were formed. Hydrogen bis-

11   triflimide was added (0.0028 g, 0.1 mmol) and the

12   mixture was heated for a further 18 hours.   Gas

13   chromatographic analysis showed that the reaction

14   was almost complete (> 99%), and gave a mixture of

15   isomers of hexadecene and tetracosene (trimer of

16   octene).   The less dense product phase was decanted

17   from the ionic / catalyst phase and purified by

18   Kugelrohr distillation at 1 mm Hg.   The ionic liquid

19   and catalyst were prepared for reuse by heating at

20   60 °C under vacuum for 1 hour.   The ionic liquid and

21   catalyst were used for further dimerisation

22   reactions of oct-1-ene without loss of activity.

23

24   **Example 21:** The Fries rearrangement of 4-

25   methylphenoxybenzoate with hydrogen and metal bis-

26   triflimide compounds.

27

28   Ytterbium(III) bis-triflimide (0.1 g) and hydrogen

29   bis-triflimide (0.01 g) was dissolved in [n-H₂₉C₁₄(n-

30   H₁₃C₆)₃P][NTf₂] (1.0 g) in a round-bottomed flask

39

1   equipped   with   a   magnetic   stirrer   and   reflux
2   condenser.   4-methylphenoxybenzoate   (1.0   g)   was
3   added.   The   mixture   was   heated   under   reflux   for   24
4   hours   at   60   °C   and   was   analysed   by   gas
5   chromatographic   analysis   as   in   previous   examples.
6   The   product   of   the   reaction   was   2-hydroxy-5-
7   methylbenzophenone   (90   %   yield).   The   isomerisation
8   of   4-methylphenoxybenzoate   to   2-hydroxy-5-
9   methylbenzophenone   is   shown   below.

10

11
12

13
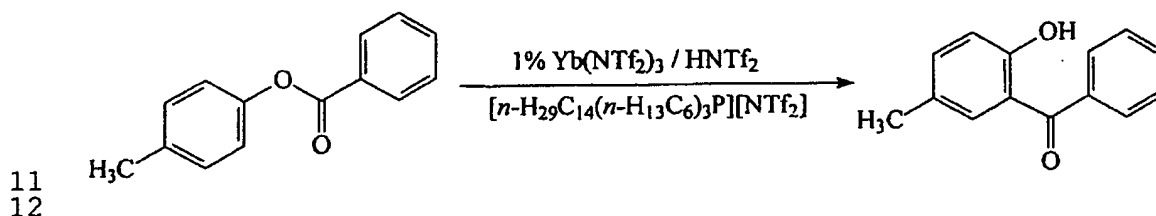
14   **Example 22:** The   reaction   of   o-xylene,   m-xylene,
15   mesitylene,   and   toluene   with   cyclohexene   with   metal
16   bis-triflimide   compounds.

17

18   In   four   separate   reaction   vessels,   ytterbium(III)
19   bis-triflimide   (0.1   g)   was   dissolved   in $[n\text{-}H_{29}C_{14}(n\text{-}$
20   $H_{13}C_6)_3P][NTf_2]$ (2.0   g)   in   a   round-bottomed   flask
21   equipped   with   a   magnetic   stirrer   and   reflux
22   condenser.   Either   o-xylene   (1.06   g,   10   mmol),   m-
23   xylene   (1.06   g,   10   mmol),   mesitylene   (1.20   g,   10
24   mmol),   or   toluene   (0.92   g,   10   mmol)   were   added   to
25   the   separate   flasks   followed   by   addition   of
26   cyclohexene   (0.82   g,   10   mmol).   The   mixtures   were
27   heated   at   80   °C   for   12   hours   and   were   analysed   by
28   gas   chromatographic   analysis   as   in   previous

1   examples. The cyclohexene peak disappeared and

2   peak(s) due to alkylation of the aromatic compound

3   and peaks due to dimerisation reactions of

4   cyclohexene were formed (see Example 26 for

5   details). The ionic liquid and catalyst were

6   prepared for reuse by heating at 60 °C under vacuum

7   for 1 hour. The ionic liquid and catalyst were used

8   for further reactions of benzene with cyclohexene

9   without loss of activity.

10

11   **Example 23**: The reaction of benzene with dodec-1-ene

12   with metal bis-triflimides, triflates and hydrogen

13   bis-triflimide.

14

15   In ten separate reaction vessels (a multi-cell glass

16   reactor with stirrers and condensers) metal

17   triflimide or metal triflate compounds (see Table

18   below) were added together with hydrogen bis-

19   triflimide (0.01 g) to $[n-H_{29}C_{14}(n-H_{13}C_6)_3P][NTf_2]$ (2.0

20   g) and stirred until the metal compound had

21   dissolved. Benzene (3.8 g, 50 mmol) and dodec-1-

22   ene (0.84 g, 5.0 mmol) were added. The mixtures

23   were heated at 80 °C for 24 hours. The excess

24   benzene was distilled off. The mixture was analysed

25   by NMR upon cooling to room temperature. The ionic

26   liquid and catalyst were prepared for reuse by

27   heating at 60 °C under vacuum for 1 hour. The ionic

28   liquid and catalyst were used for further reactions

29   of benzene with dodec-1-ene without loss of

30   activity. The results are shown in Table 8 below.

1   **Table 8**

Compound	Mass / g	Unreacted dodecene	Isomerised dodecene	Dodecyl benzene
$Yb(NTf_2)_3$	1.02	0	0	100
$Co(NTf_2)_2$	0.62	0	99	1
$Cu(NTf_2)_2$	0.62	0	1	99
$Pb(NTf_2)_2$	0.76	0	100	0
$In(NTf_2)_3$	0.95	0	0	100
$Ga(NTf_2)_3$	0.63	0	61	39
$Zn(OTf_2)_2$	0.36	67	33	0
$Cu(OTf_2)_2$	0.36	1	96	3
$Yb(OTf_2)_3$	0.53	0	91	9
$La(OTf_2)_3$	0.59	0	60	40

2

3   **Example 24:** The reaction of toluene with benzoyl

4   chloride with metal compounds dissolved in

5   [bmim][NTf₂].

6

7   In five separate reactions, either titanium(IV)

8   chloride (1 mol %) or tin(IV) chloride (1 mol %), or

9   tungsten(VI) chloride, or hafnium(IV) chloride or

10   palladium(II) chloride was added to 1-butyl-3-

11   methylimidazolium   bis-trifluoromethanesulfonimide

12   ([bmim][NTf₂]) (2.0 g) 25 cm^3 in a round-bottomed

13   flask equipped with a magnetic stirrer and reflux

14   condenser, and the toluene (2.81 g, 30 mmol) and

15   benzoyl chloride (2.84 g, 20 mmol) were added. The

16   mixtures was heated under reflux for 24 hours and

17   was analysed by gas chromatographic analysis as in

18   previous examples. The conversion of starting

42

1 materials to methylbenzophenone was quantitative
2 except for the palladium(II) catalysed reaction (75
3 % yield). The variation of yield with time in the
4 reaction of several new metal bis-triflimide salts
5 in the reaction of benzoyl chloride with toluene in
6 given in Figure 4. These reactions were performed
7 in parallel, and the yields were determined by GC
8 analysis.
9
10 In this invention, the use of a metal halide
11 dissolved in a bis-triflimide ionic liquid can be
12 used for reactions such as the Friedel-Crafts
13 reactions. This is useful where a particular metal
14 bis-triflimide salt is difficult to prepare or
15 isolate. In this invention, five metal halides
16 (chlorides) (1 mol % with respect to the reactants)
17 were dissolved in [bmim][NTf$_2$]. This combination
18 was used to catalyse the reaction of toluene with
19 benzoyl chloride to give methylbenzophenone. The
20 yield with respect to time is given in Figure 4.
21 All of the metals chosen gave the expected products
22 in good yield, but the combination of 1% mol tin(IV)
23 chloride in [bmim][NTf$_2$] was a particularly
24 effective catalyst. This process of using metal
25 compounds dissolved in an ionic liquid (usually bis-
26 triflimide) can also be used with compounds of other
27 metals (particularly transition metals (d-block) or
28 f-block metals)) not listed in Figures 3 or 4.
29
30 **Example 25**

1 A number of aromatic sulfonylation reactions were

2 performed.   These reactions are very similar to

3 Friedel-Crafts acylation reactions and are performed

4 under similar conditions.   The key difference is

5 that a $-SO_2-X$ group replaces a $-CO-X$ (X = leaving

6 group).   In   most   cases,   the   selectivities,

7 reactivities and yields were found similar to the

8 corresponding acylation reaction.   The reaction of

9 sulfuryl chloride with benzene resulted in the

10 formation of chlorobenzene (quantitatively) and SO_2.

11 This is as is found in many other reactions of SO_2Cl_2

12 with   aromatic   compounds   performed   in   molecular

13 solvents.

14
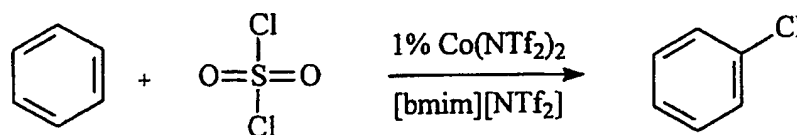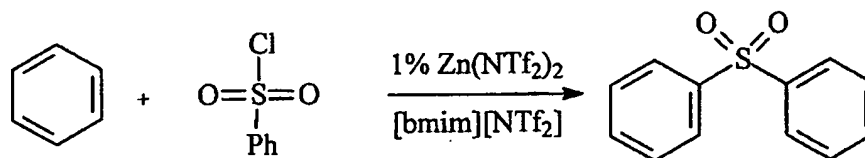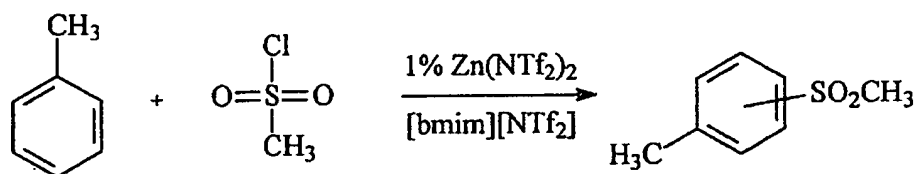
15
16

17 **Example 26**

18 The alkylation of various aromatic compounds with

19 cyclohexene in a phosphonium ionic liquid with 10 %

20 ytterbium(III)   bis-triflimide   with   a   trace   of

1   hydrogen bis-triflimide were carried out. A side

2   reaction also takes place that results in the

3   formation of a dimer of cyclohexene (see below) and

4   this results in a slight reduction in the yield of

5   the Friedel-Crafts reaction. However, is should be

6   noted that this demonstrates that metal triflimide

7   compounds can be used for dimerisation and

8   oligomerisation reactions.

9
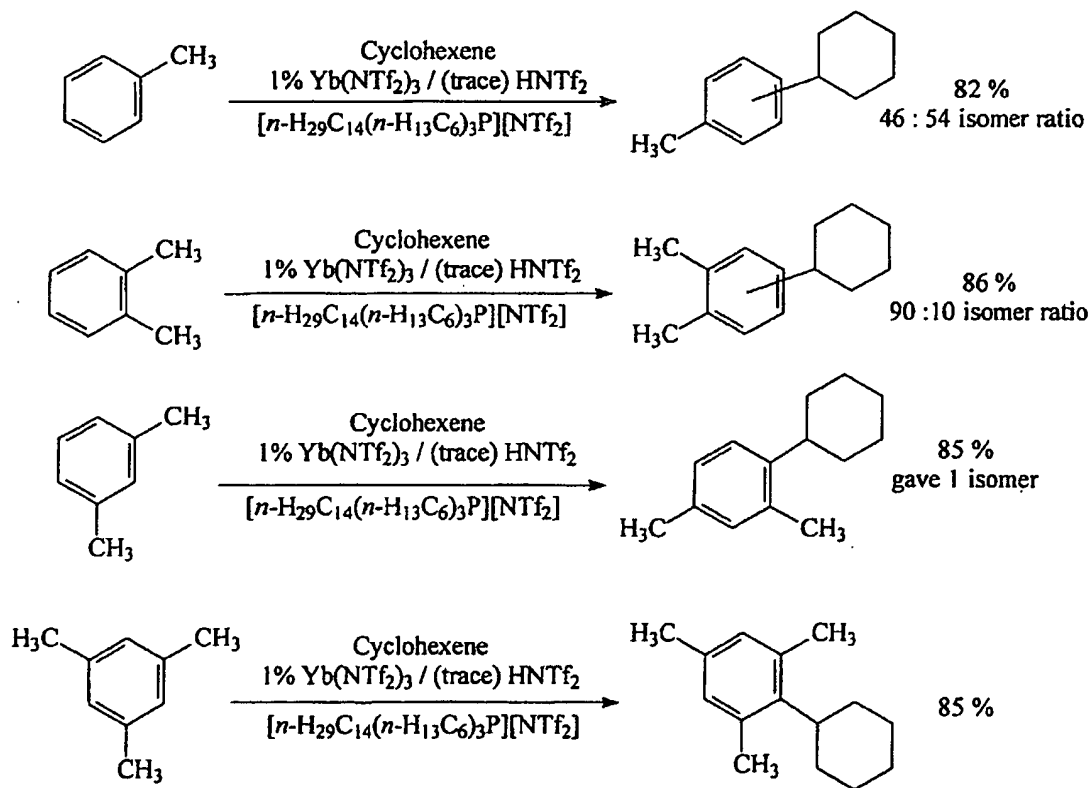
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12   The reaction of aromatics with cyclohexene in a

13   phosphonium ionic liquid for 12 hours at 80 °C is

14   shown above. Below is shown the dimerisation of

15   cyclohexene.

1
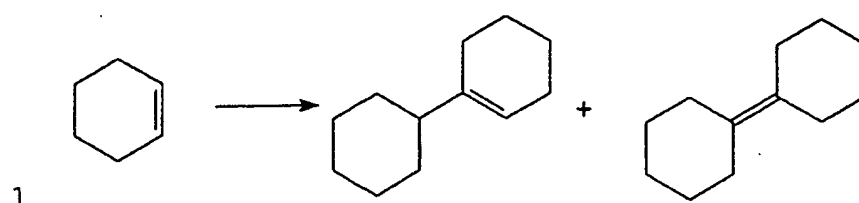
1   **CLAIMS**

2

3   1.   A process for carrying out a chemical reaction

4   which is catalysed by one or more metal or hydrogen

5   fluoroalkylsulfonylated   compound   which   process

6   comprises carrying out said reaction in the presence of

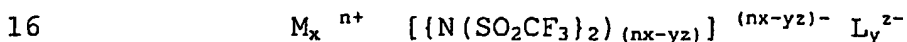7   an ionic liquid or in solvent-free conditions.

8

9   2.   A process as claimed in claim 1 wherein the one or

10   more metal or hydrogen fluoroalkylsulfonylated compound

11   is a metal or hydrogen bistriflimide compound.

12

13   3.   A process according to claim 2 wherein the

14   bistriflimide compound has the following formula:

15

16   M_x^{n+} $[\{N(SO_2CF_3)_2\}_{(nx-yz)}]^{(nx-yz)-}$ L_y^{z-}

17

18   where M is hydrogen or a metal;

19   L is a negative or neutral ligand;

20   n is 2,3,4,5,6,7 or 8;

21   x is greater than or equal to 1;

22   y is 0,1,2,3,4,5,6,7or 8; and

23   z is 0, 1,2,3 or 4.

24

25   4.   A process according to any one of the preceding

26   claims wherein M is a metal selected from the metals in

27   groups 1 to 16 and the lanthanides and the actinides.

28

29   5.   A process according to any one of the preceding

30   claims wherein the chemical reaction is one of :

31   (a)   an electrophillic substitution reaction, or

1   (b)   an   isomerisation,   polymerisation   or
2   rearrangement   of   a   chemical   compound   or
3   molecule.
4   6.   A process according to claim 5 wherein the
5   chemical reaction is a reaction between an aromatic
6   compound and an alkylating, acylating or sulfonating
7   agent.
8
9   7.   A process according to claim 5 wherein the
10   chemical reaction is a rearrangement of esters of
11   phenols to acyl phenols.
12
13   8.   A process according to any one of the preceding
14   claims which comprises carrying out said reaction in
15   solvent free conditions wherein the one or more metal
16   or hydrogen fluoroalkylsulfonylated compound is added
17   directly to the reactants.
18
19   9.   A process according to any one of the preceding
20   claims which comprises carrying out the reaction in the
21   presence of an ionic liquid which comprises dissolving
22   or suspending the one or more metal or hydrogen
23   fluoroalkylsulfonylated compound in an ionic liquid.
24
25   10.   A process according to claim 9 wherein the ionic
26   liquid comprises a cation chosen from 1-alkylpyridinium
27   or 1,3-dialkylimidazolium cation, alkyl- or poly-
28   alkylpyridinium, alkyl or poly-alkylimidazolium, alkyl
29   or poly-alkylpyrazolium, alkyl or poly-alkyl ammonium,
30   alkyl or poly-alkyl phosphonium and alkylated

1   diazabicyclo-[5,4,0]-undec-7-ene; and an anion chosen

2   from bis-trifluoromethanesulfonimide,

3   bis-pentafluoroethanesulfonimide,

4   hexafluorophosphate(V), tetrafluoroborate(III),

5   trifluoromethanesulfonate, cyanamide, fluoro or

6   perfluoroalkylsulfonate, halide, sulfate,

7   hydrogensulfate, alkylsulfate, alkylsulfonate,

8   arylsulfate, arylsulfonate, nitrate, carboxylate,

9   phosphate, hydrogenphosphate, dihydrogenphosphate,

10 alkylphosphate, alkylphosphonate, phosphonate, nitrite,

11 arsenate, antimonate, haloaluminate, aluminate, borate,

12 silcate, haloindate(III), gallate, alkylborate and

13 halogallate.

14

15 11. A process according to any one of the preceding

16 claims wherein the catalyst or the catalyst and ionic

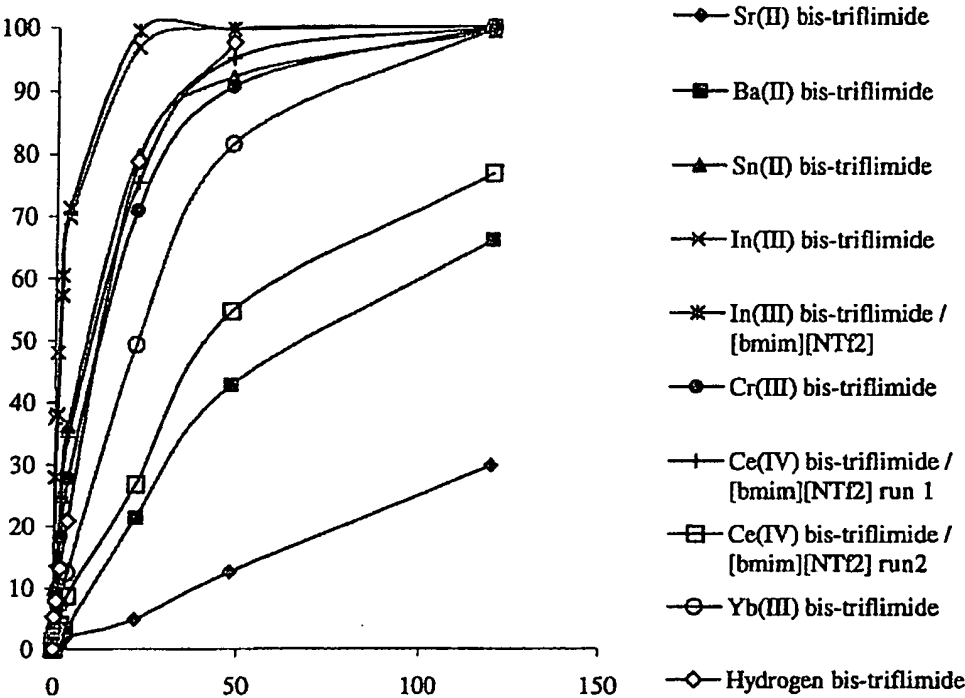17 liquid combination are subsequently separated from the

18 reaction mixture.

19

20 12. A process according to claim 11 wherein the

21 catalyst or the catalyst and ionic liquid combination

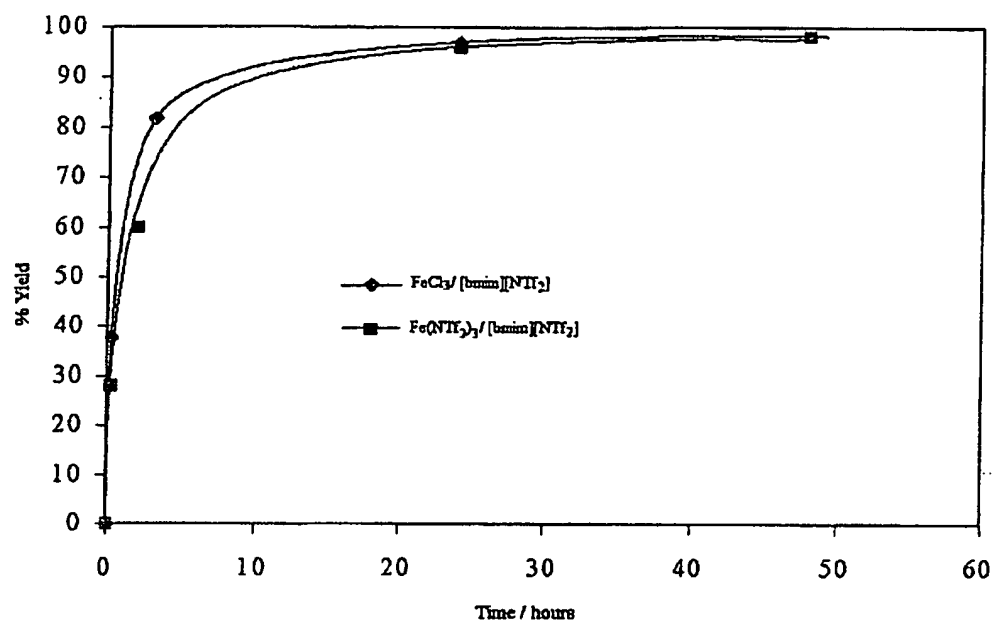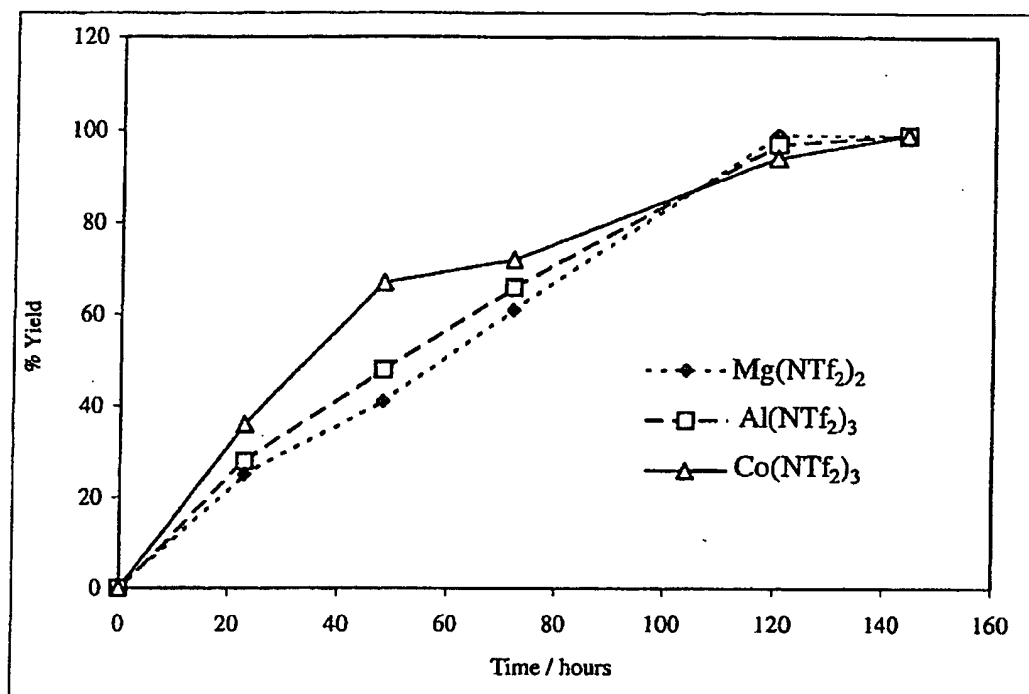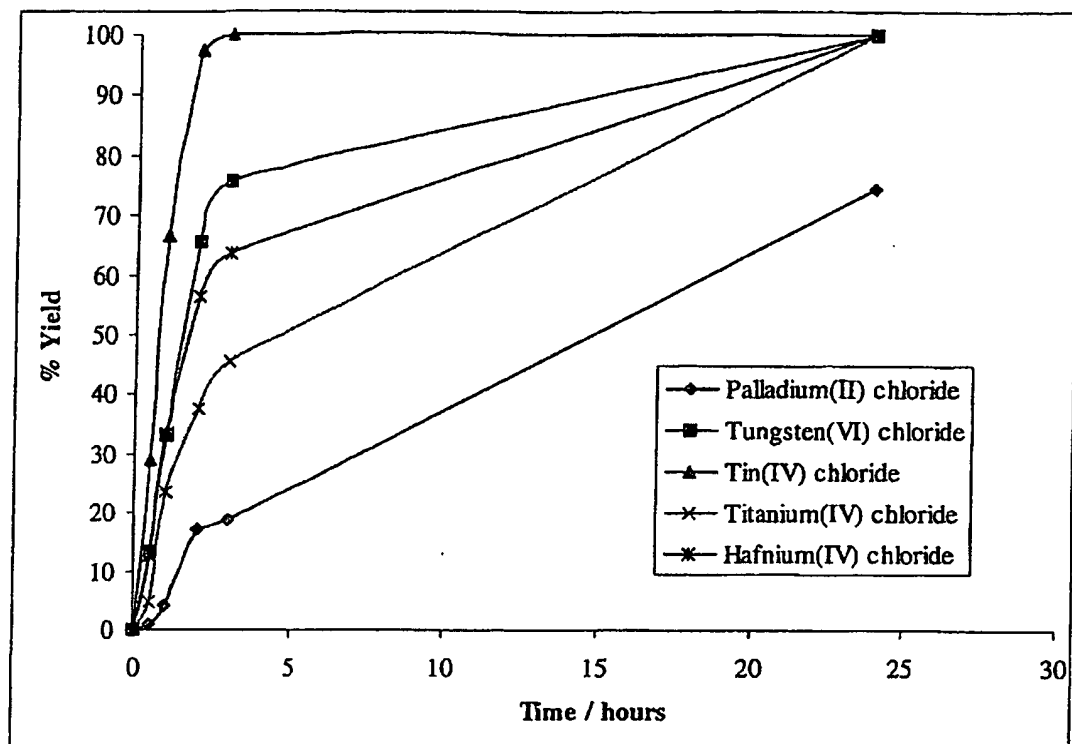22 are subsequently recycled.

23

1 **Figure 1**

2

Legend:
- Sr(II) bis-triflimide
- Ba(II) bis-triflimide
- Sn(II) bis-triflimide
- In(III) bis-triflimide
- In(III) bis-triflimide / [bmim][NTf2]
- Cr(III) bis-triflimide
- Ce(IV) bis-triflimide / [bmim][NTf2] run 1
- Ce(IV) bis-triflimide / [bmim][NTf2] run2
- Yb(III) bis-triflimide
- Hydrogen bis-triflimide

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1   Figure 2

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1 **Figure 3**

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1   **Figure 4**

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